



AFRL-OSR-VA-TR-2015-0115

ATTOSECOND ELECTRON PROCESSES IN MATERIALS

Stephen Leone
REGENTS OF THE UNIVERSITY OF CALIFORNIA THE

05/19/2015
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
04/30/2015		Final		05/01/2014 - 04/30/2015	
4. TITLE AND SUBTITLE Attosecond electron processes in materials: science of excitons, plasmons, and charge dynamics			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER FA9550-10-1-0195		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Stephen R. Leone			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Regents of the University of California, University of California, Berkeley Sponsored Projects Office 2150 Shattuck Avenue, Suite 313 Berkeley, CA 94704-5940				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Evelyn Dohme Program Officer, NSSEFF Air Force Office of Scientific Research 875 N Randolph St, Ste 325, Rm 3112 Arlington, VA 22203-1768				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Stephen R. Leone
Unclassified	Unclassified	Unclassified	Unclassified		19b. TELEPHONE NUMBER (Include area code) 510-643-5467

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATE COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33315-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report. e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

Final Report

Attosecond Electron Processes in Materials: Excitons, Plasmons, and Charge Dynamics

National Security Science and Engineering Faculty Fellowship

Department of Defense

Office of Assistant Secretary of Defense for Research and Engineering

Stephen R. Leone (University of California, Berkeley)

Grant #: FA9550-10-1-0195

Reporting Period: 1 May 2010 - 30 April 2015

Abstract:

A five year program focusing on investigation of attosecond electron dynamics in solid state materials is completed. Two experimental apparatuses for attosecond time-resolved extreme ultraviolet (XUV) studies were constructed. Highlights of results are: a 450 attosecond electronic response time in the conduction band of silicon was experimentally measured by observing steps in the $L_{2,3}$ -edge spectrum of silicon, synchronized with the excitation laser electric field. Independent electron and hole dynamics were observed in germanium by time-resolved ultrafast measurements on the $M_{4,5}$ -edge spectrum of germanium. A near-instantaneous spectral response over a broad range around the vanadium $M_{2,3}$ -edge, followed by a fast reshaping of the spectrum, was observed in VO_2 , suggesting a signature of the ultrafast insulator to metal transition.

Introduction:

The goal of this work was to understand the generation, transport, and manipulation of electronic charge carriers, multi-electron motion and dynamical electron correlations together with corresponding electronically induced excitations and phase transformations in solid state systems [1]. To study these processes, two specialized experimental setups were built. The constructed apparatuses utilize short visible laser pulses (4-7 fs) together with extreme ultraviolet (XUV) attosecond pulses at controlled time delay with attosecond time resolution. In general, the visible pulse serves as an excitation pulse that induces a rapid change in the electronic density. The XUV pulse serves as a chemically sensitive probe pulse utilizing specific core level transitions in atoms that are part of a material under study. The measurements follow electronic modification

of the energy levels and corresponding transition probabilities in these structures by analyzing the extremely rapid changes in the transient absorption of specific elements in the materials.

The research that was performed during this program is based on previous knowledge and experiments in the Leone group. The group combined attosecond transient absorption methods [2, 3] that were developed and demonstrated in gas phase atomic media together with the experience that was gained during investigations of $M_{2,3}$ -edge spectroscopy of transition-metal oxides with femtosecond resolution [4].

During the program time, two experimental apparatuses for time-resolved extreme ultraviolet studies with attosecond resolution were constructed. Each apparatus (see one example in Fig. 1) includes a carrier-envelope phase stabilized laser system producing ~ 500 μJ pulses with 5 fs duration near 750 nm, a high harmonic generation chamber, a focusing chamber, and XUV transient absorption and photoelectron experimental chambers. These systems were built using funds from the NSSEFF DoD with additional support from the W.M. Keck Foundation. Production of isolated attosecond pulses has been established for both instruments.

The highlights of the results that were obtained using the two apparatuses are the following. First, a tunneling effect in silicon was experimentally verified by observing sharp steps in the extreme ultraviolet (XUV) Si $L_{2,3}$ -edge spectrum synchronized with the excitation laser electric field [5]. The electronically induced modifications in the conduction band occur on 450 attosecond timescales. These are the first attosecond-resolved experiments in a semiconductor band gap material, and they illustrate the unprecedented temporal resolution of electron dynamics and new findings that can be obtained using the XUV transient absorption method. Second, ultrafast band dynamics as well as independent electron and hole dynamics were observed in germanium by time-resolved study of the Ge $M_{4,5}$ -edge spectrum. Third, a near-instantaneous spectral response over a broad range around the vanadium $M_{2,3}$ -edge, followed by a fast reshaping of the spectrum was observed in VO_2 , suggesting an ultrafast insulator to metal transition. Fourth, theoretical modeling was performed to predict possible attosecond measurements where an attosecond XUV pulse is used to eject electrons from a metal nanosphere in which a plasmon has been excited by a few-cycle optical pulse [6].

Current and future utilization of the experimental setups that were built using NSSEFF DoD funds involve possible explorations of the insulator to metal transition in the magneto-resistive material $\text{Pr}_x\text{Ca}_{1-x}\text{MnO}_3$, study of the charge carrier transport mechanism in perovskite type solar materials, carrier dynamics in gallium arsenide thin films, and real time investigations of plasmon dynamics in SiO_2 covered gold nanospheres. Moreover, the accomplishments that were made possible through this program led to additional funding being awarded to the Leone group through the DARPA PULSE, ARO MURI, and AFOSR MURI programs. A goal of future programs is to construct an attosecond-attosecond system in collaboration with Prof. Zenghu Chang at the University of Central Florida and Prof. Paul Corkum at the University of Ottawa

(DARPA PULSE) and to investigate ultrafast electron dynamics in condensed matter with next generation attosecond X-ray sources (AFOSR MURI) in collaboration with Pierre Agostini, and Louis F. DiMauro from Ohio State University, Daniel M. Neumark from University of California, Berkeley, Mark I. Stockman from Georgia State University, Paul B. Corkum from University of Ottawa, Canada and Ferenc Krausz from Ludwig Maximilian University of Munich, Germany. Below, the highlights of several results are described in more detail.

Scientific and Technical Achievements and Findings:

1. Table-top systems for time-resolved core-level spectroscopy with attosecond time resolution for condensed matter studies

One of the two experimental systems that were built during the project duration using the funds from the NSSEFF DoD with additional support from the W.M. Keck Foundation is shown in Fig. 1. Both systems include very similar design considerations that are described below. The main goal of the apparatus is to resolve sub-cycle charge dynamics upon photo-excitation in condensed matter systems.

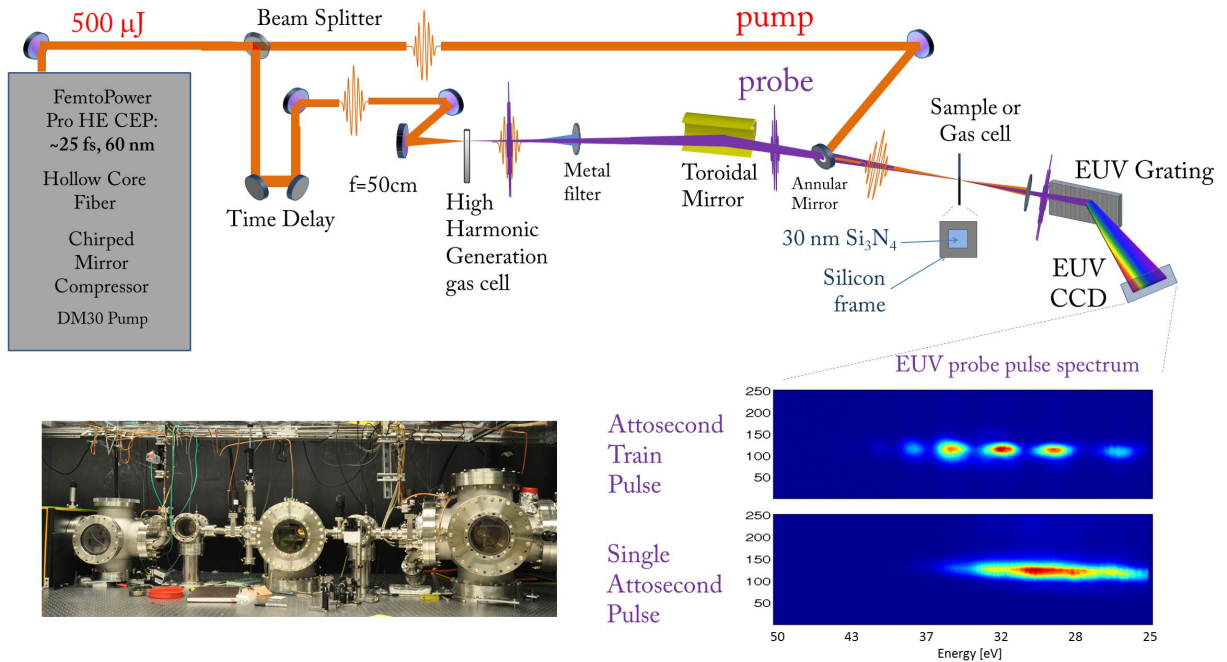


Figure 1: Experimental Setup. The experimental system starts with a commercial Carrier-Envelope Phase (CEP) stabilized Ti:sapphire amplified laser system. The outer arm is the visible pump pulse which initiates the electron excitation. The inner arm is used to generate the isolated attosecond probe pulse. Following the XUV generation the residual visible light of the probe arm is filtered out. The outer visible pump and inner XUV probe pulses are focused into the sample usually deposited on a 30 nm thick Si₃N₄ substrate. Following the interaction region, the

pump pulse is filtered out while the attosecond XUV probe propagates further and is spatially dispersed onto an XUV CCD camera. The time dependent XUV absorption spectra are recorded as a function of the time delay.

In general, the experimental XUV transient absorption setup begins with a commercial 1 kHz Ti:sapphire carrier envelope stabilized (CEP) amplifier system (Femtopower Compact Pro). The 25 fs pulses with 1.5 mJ energy at the output are focused using a $f=1.5$ m lens into a 250 micron hollow core fiber (HCF) filled with neon gas at atmospheric pressure to stretch the pulse spectrum from 60 nm FWHM centered at 800 nm into a ~ 180 nm FWHM spectrum centered at 780 nm. Following the HCF the 0.5 mJ pulses are re-collimated using a $f=1.5$ m mirror into a dispersion compensation (DC) setup consisting of 4 pairs of PC70 chirped mirrors. The setup is optimized to compensate for the 4 m of air that the beam travels from the exit of the HCF and the entrance window of the vacuum chamber, the 0.5 mm fused silica (FS) entrance window, the 1 mm beam splitter positioned at 45° and a pair of FS wedges to deliver 5 fs pulses to the front of the vacuum chamber.

Following the DC, 0.5 mJ pulses are split using a beam splitter with a 80/20 ratio. The transmitted part is focused with a $f=50$ cm focal length mirror into a 4 mm length gas cell filled with krypton, argon or neon to produce either a short train of isolated attosecond pulses or an isolated attosecond pulse (IAP), with various energy ranges from 25 eV to 120 eV. The XUV generation mechanism utilizes the process of High Harmonic generation (HHG) [7]. One difference between the two experimental systems that were built is in the frequency range of the XUV attosecond pulse and the corresponding process of creating an IAP during the HHG process. While one system is optimized to operate in the 30 eV-50 eV range by implementing the Double Optical Gating technique [8], the other system is optimized to operate in the 60 eV-120 eV range by implementing the intensity gating technique. Following the HHG generation, the residual visible pulse is blocked using a 200 nm aluminum or zirconium foil. The remaining XUV pulses are focused into a 100 micron spot size in the interaction region using a 10° grazing incidence toroidal mirror (ARW optical corporation) with a 1m to 1m focal plane projection ratio. After the interaction region the XUV pulses are focused in the vertical plane and spectrally dispersed in the horizontal plane using a variable line spaced grating into a CCD camera (PIXIS 400B). The reflected part of the beam is focused using a $f=1$ m mirror into a 150 mm spot size in the interaction region and spatially overlapped with the XUV pulse in a collinear geometry using a 45° 2 mm hole mirror located ~ 0.5 m before the interaction region. The relative delay between the pump and the probe pulses is controlled using a piezo stage. Following the interaction region the visible femtosecond pump pulse is blocked using a 200 micron pin hole followed by an additional 200 nm metal filter.

Finally, the time dependent XUV absorption spectra are recorded as a function of the delay between the visible few femtosecond pulse and the IAP pulse. In addition to the unprecedented time resolution, the XUV spectrum of the IAP pulses coincides with many core level transitions for elements, such as first row transition metals, silicon, and germanium, allowing a time-

resolved variant of x-ray absorption near-edge structure spectroscopy (XANES) [7]. The experimental apparatuses that were built using the NSSEFF DoD funding are very versatile and may be adapted for future experiments to study fast electronic responses in a variety of materials with chemical charge and elemental sensitivity on the attosecond to femtosecond timescales.

2. Attosecond Dynamics in Silicon.

Initial steps of the excitation of electrons from valence band (VB) states into mobile conduction band (CB) states were investigated for the first time using attosecond solid-state spectroscopy in real time in silicon [5]. The main finding of this study indicates that electrons injected into the conduction band by few-cycle laser pulses alter the silicon XUV absorption spectrum in sharp steps synchronized with the laser electric field oscillations. The observation of a ~ 450 -attosecond step rise time during the excitation process provides an upper limit for the carrier induced band-gap reduction timescale. Quantum dynamical simulations using time-dependent density functional theory (TD-DFT) interpret the carrier injection step as light-field-induced electron tunneling. This electronic response is observed to be followed by a slower lattice motion with a longer time constant of 60 femtosecond, resembling the period of the fastest optical phonon in silicon.

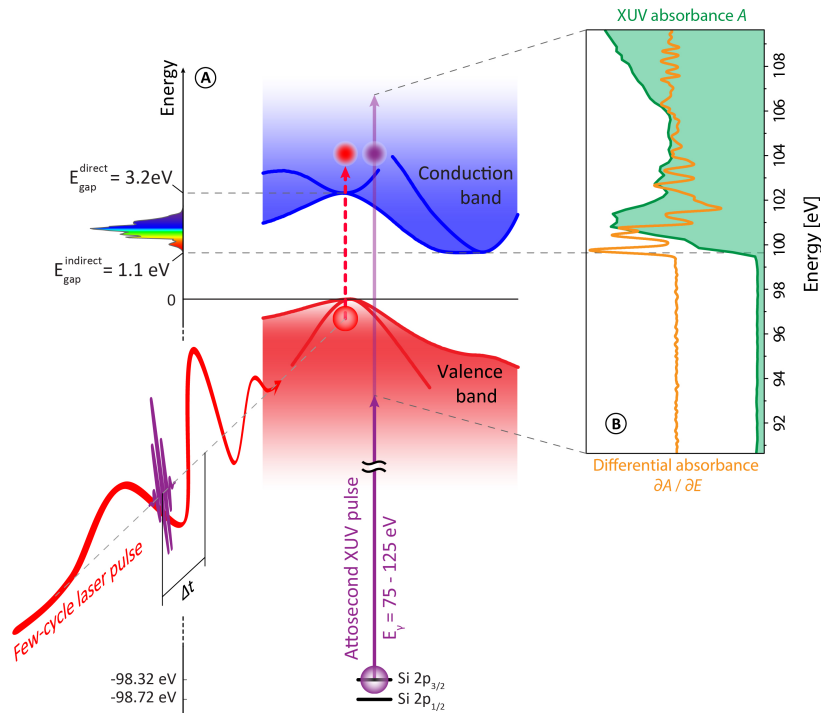


Figure 2: Ultrafast spectroscopy of band-gap dynamics. (A) An intense few-cycle laser pump pulse with a spectrum covering the entire visible wavelength range excites electrons into the conduction band, where they are probed by an

attosecond XUV probe pulse. Changes in the electronic population of the conduction band are revealed as modifications of the silicon L-edge absorbance A and its derivative $\partial A/\partial E$ (B). By varying the time delay Δt between the two pulses, dynamic changes to the L-edge spectrum can be tracked and translated into the evolution of the conduction band population.

The principles of attosecond transient absorption spectroscopy of semiconductors, which were developed under this project, are illustrated in Fig. 2 (reprinted from [5]). Attosecond pulses tuned to the silicon $L_{2,3}$ edge centered at 99 eV, are used to measure the dynamics of electrons injected into the CB by few-cycle, intense near-infrared NIR laser pump pulses. The probe pulses are shorter than 100 attoseconds, as confirmed by photoelectron streaking spectroscopy and span a spectrum of XUV photon energies covering 80 to 125 eV. The corresponding streaking trace is shown in Fig. 3 (reprinted from [5]).

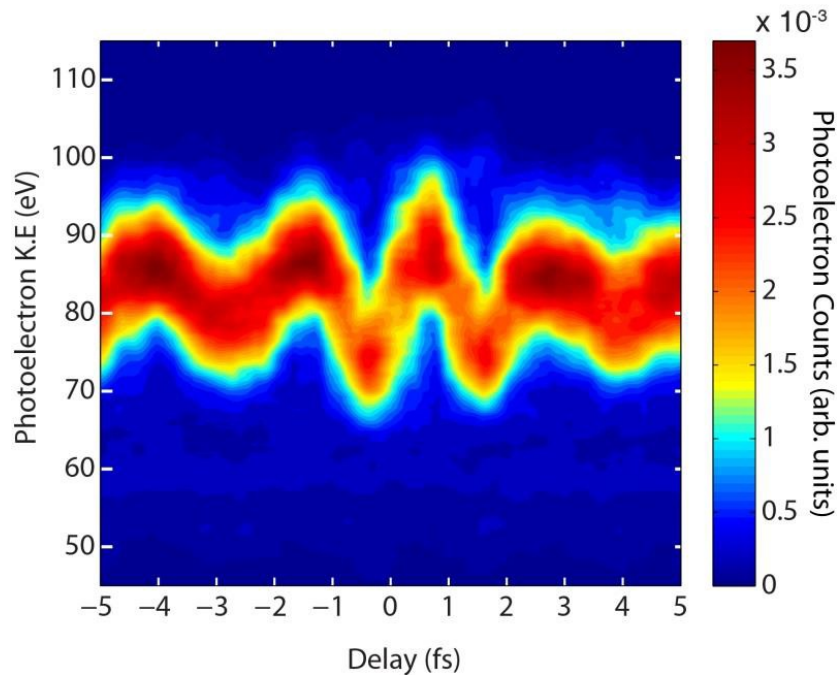


Figure 3: Photoelectron kinetic energy acquired by inserting a Pd XUV filter in the attosecond pulse beam; the signal results from momentum shifting of photoelectrons of directly ionized neon atoms along the direction parallel to the electric field of the streaking laser pulse, plotted against the time delay between the ionizing XUV pulse and the streaking electric field.

Fig. 2 (B) shows the recorded silicon L-edge absorbance A of a 250-nm-thick single crystalline free-standing silicon membrane in the $\langle 100 \rangle$ orientation, as well as the derivative of the static absorbance $\partial A/\partial E$ as a function of the XUV photon energy computed from the raw data, which facilitates assessment of excitation-induced broadening and shifts of the CB features. Whereas the initial state of the electron undergoing the XUV probe transition is a 2p core orbital, the final state of both the XUV probe and the NIR pump excitation lies within the CB manifold. Electron interactions in the CB alter the XUV transition, thus rendering the attosecond XUV absorption.

The laser-induced transfer of electrons to the CB results in a wealth of modifications to the XUV transition. Fig. 4 (A) displays the derivative of the L-edge absorbance spectrum, $\partial A/\partial E$, as a function of time delay Δt between the NIR pump and the XUV-probe pulses. Excitation of silicon by a few-cycle intense NIR laser pulse results in a global broadening of the L-edge substructures. Most important, as seen in Fig. 4 (B), the spectrum recorded with carrier-envelope-phase (CEP) stabilized NIR pump pulses evolves with a step like behavior synchronized with the half-cycle period of the pump electric field oscillations, indicative of sub-femtosecond population transfer. Further, an effective reduction of the measured band gap (band-gap narrowing) after the excitation is observed (Fig. 4 (C), blue line), and during the excitation pulse, a transient field-induced blue shift of the L-edge onset is recorded (Fig. 4 (C), red line). Finally, Fig. 4 (D) shows a clear bi-exponential decay of the signal recorded over an extended delay range with time constants of 5 fs (laser pulse limited, steps resolved in 450 as) and 60 fs, respectively, indicating the transition between purely electronic initial response after the laser pulse and convoluted electronic-lattice dynamics at longer time scales.

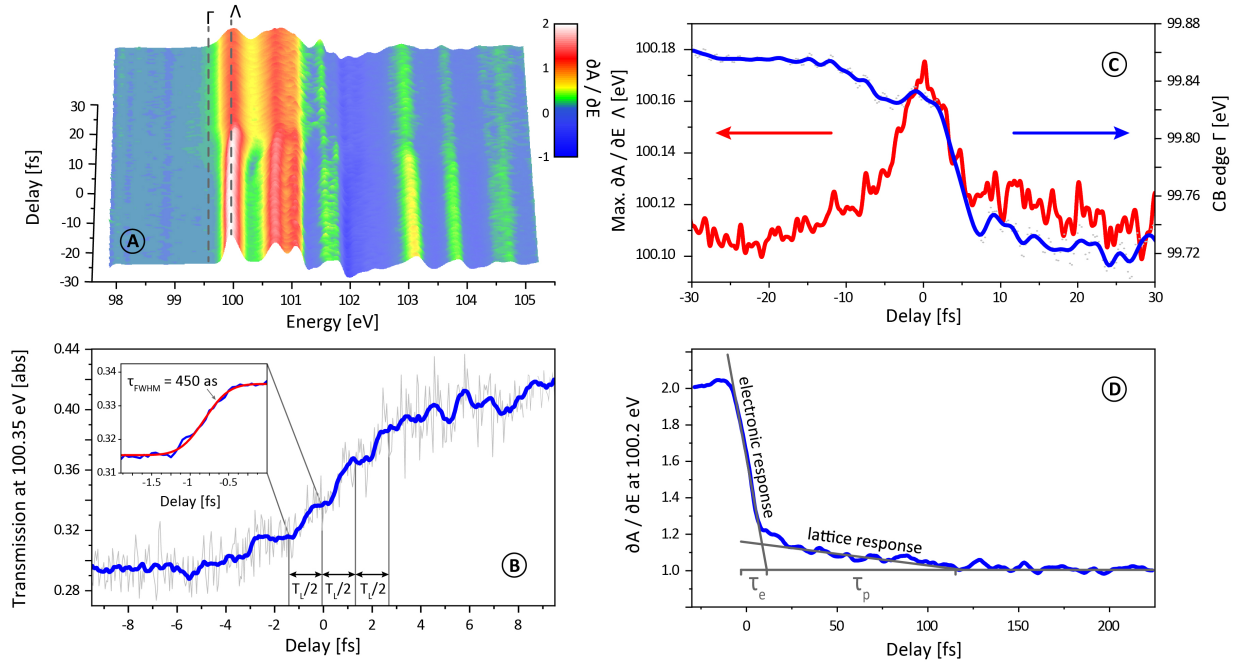


Figure 4: Attosecond transient absorption spectroscopy of silicon. (A) The injection of electrons into conduction band states of silicon by a few cycle near-infrared laser pump-pulse modifies the derivative of the XUV absorbance $\partial A/\partial E$ plotted as a function of probe-photon energy and time delay between pump and probe pulse. The color scale represents the value of $\partial A/\partial E$. (B) A close-up of the temporal evolution of the XUV transmission at 100.35 eV reveals the increase of the signal amplitude in sharp steps synchronized with the laser electric field oscillations. The inset shows a fit to evaluate the step rise time (450 as). The blue line is a rolling average of the raw signal depicted in gray. (C) The position in energy of the first peak of the derivative [marked Λ in (A)] is plotted (red), along with the energy of the L-edge onset (marked Γ) evaluated at $\partial A/\partial E = 0.2$ (blue). (D) tracks the amplitude of $\partial A/\partial E$ at

100.2 eV, the position of the maximum $\partial A/\partial E$ before excitation. The straight lines indicate the different time scales over which electronic (t_e) and nuclear (t_p) dynamics occur.

3. Electron Dynamics in Germanium Thin Films

Complex electronic dynamics following an excitation of carriers from the valence band to conduction band by an intense few cycle visible pulse are measured using tabletop transient absorption XUV spectroscopy with a few femtosecond resolution. The schematic excitation pathway together with $M_{4,5}$ – edge absorption spectra are presented in Fig. 5. A poly-crystalline 100 nm thick germanium sample, which is deposited onto a 30 nm silicon nitride substrate, is illuminated with a 5 fs visible pulse. The electron dynamics resulting from ultrafast population transfer induces changes in both the valence and conduction bands of germanium. Unlike the silicon experiments, which only probed the conduction band, it is experimentally demonstrated that one photon XUV transitions from the 3d state of germanium are sensitive to both the valence and conduction band carrier density populations, and there are corresponding changes to the structure of both bands as a result of the light-induced carrier transfer.

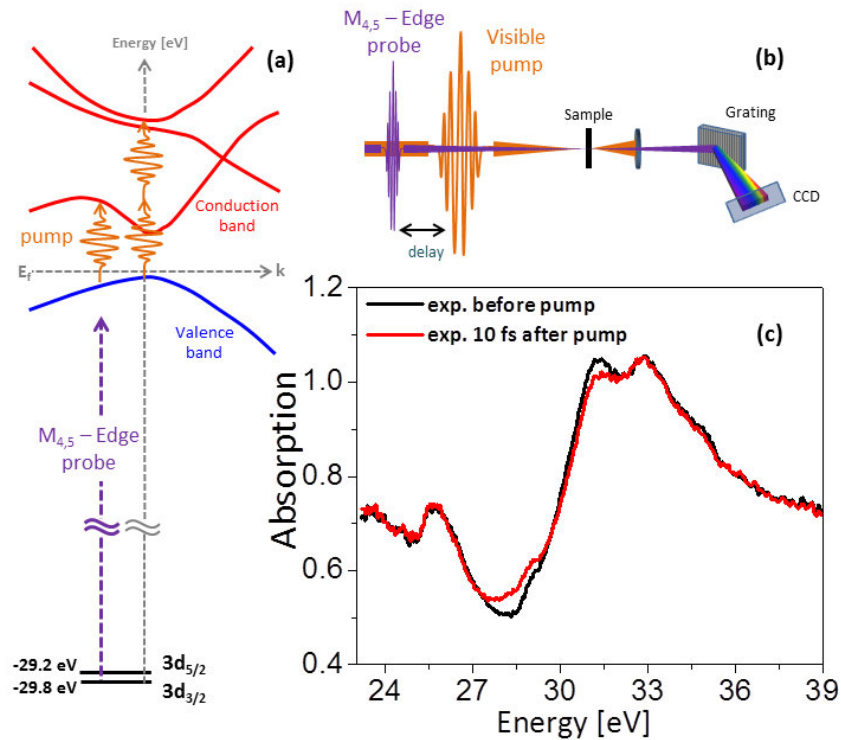


Figure 5: (a) Pump-probe excitation diagram and schematic electronic band structure of germanium. (b) Schematic representation of femtosecond $M_{4,5}$ - Edge absorption spectroscopy. (c) Germanium $M_{4,5}$ - edge absorption spectrum at negative delay (black) and at $\tau=10$ fs (red).

Figure 6 (a) presents a differential absorption spectrum of the $M_{4,5}$ edge of germanium as a function of the probe pulse energy and pump-probe delay. The almost instantaneous change in the absorption spectrum in the vicinity of the Fermi level suggest fast electronic driven response of the conduction and valence band energies and occupancies as a result of carrier excitation. Fast increase in the absorption below the Fermi edge (see Fig. 6 (b)) is followed by a slow lattice driven response. In the case of the spectral region above the Fermi level, absorption bleaching is observed, followed by fast spectral recovery.

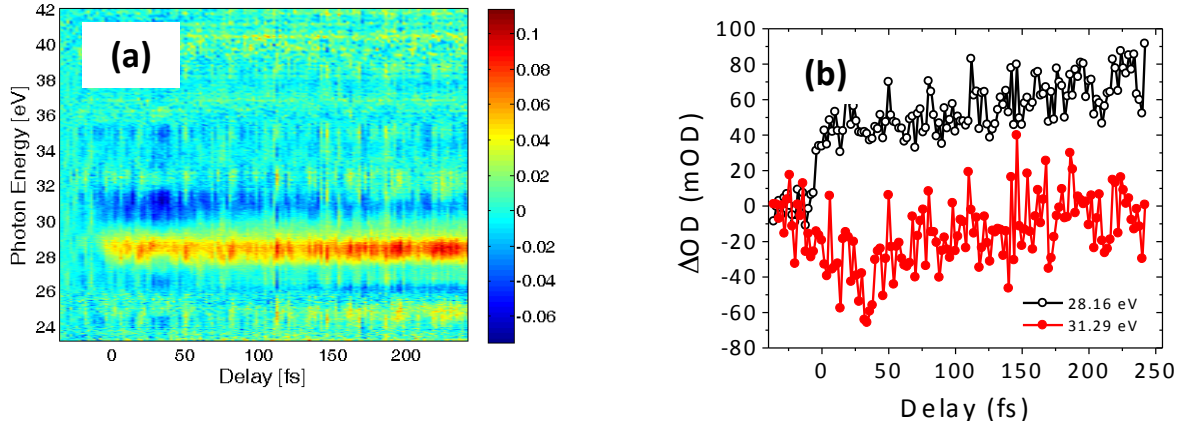


Figure 6: (a) Differential absorption spectrum of the $M_{4,5}$ edge of germanium as a function of the probe pulse energy and pump-probe delay. The presented absorption spectra are normalized to the absorption at negative delay, showing absorption bleaching above the Fermi level (30 eV) and increased absorption above the Fermi level. (b) Differential absorption as a function of the pump probe delay at 28.16 eV (black) and 31.29 eV (red).

4. Transient Absorption Spectroscopy of an Insulator-to-Metal Phase Transition Material: Vanadium Dioxide

Changes in the vanadium 3p core level spectrum were observed with attosecond transient absorption upon excitation of carriers into the 3d conduction band of vanadium dioxide (VO_2) using few cycles NIR pulses. By observing ultrafast photo-induced changes to the spectrum (see Fig. 7), measurements are sensitive to the rapid rearrangements in the density of states that can result from strong electron correlation and the insulator to metal phase transition (IMT). VO_2 displays a near-instantaneous spectral response over a broad range around the vanadium M-edge, followed by a fast reshaping of the spectrum. The fast and persisting rise in absorbance at the Fermi level is suggestive of transition to a metallic phase, and the non-congruence of the fast spectral response with thermally induced changes hints at the importance of intermediate states in mediating the material's photo-induced response.

To gain access to the dynamics and changes in electronic structure that occur both before and after the lattice has time to respond, attosecond transient absorption measurements are performed

on solid state VO_2 thin films. The IMT is initiated by a few-femtosecond carrier-envelope-phase stabilized NIR pulse (5 fs FWHM, 760 nm central wavelength). The absorption of a time-delayed, collinearly propagating attosecond pulsed light source (produced by high harmonic generation in argon) is measured around the vanadium M-edge with an extreme ultraviolet (XUV) spectrometer. Static M-edge spectra are measured for both insulating and thermally induced metallic phases and compared with the photoinduced changes.

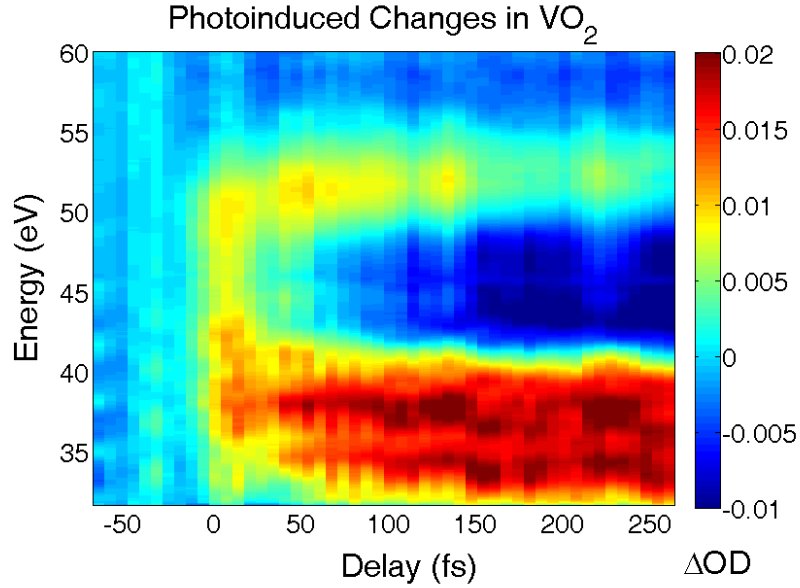


Figure 7: Transient changes in the XUV absorption spectrum of VO_2 , showing a fast increase in absorbance, followed by a redistribution of the spectral weight.

As presented in Fig. 7, in the transient measurements, a fast rise in absorbance is observed across a broad spectral range surrounding the vanadium 3p M-edge at 40 eV, which appears during the NIR laser field within less than 10 fs. On longer timescales, on the order of 150 fs, a bleach is observed in the spectrum above the M edge, and an increase is observed at and below the Fermi level (located at 40 eV relative to the vanadium 3p core level transition that is probed). The increased spectral weight at the Fermi level is a common feature of both the heating induced and photoinduced responses, which is suggestive of a transition to a metal.

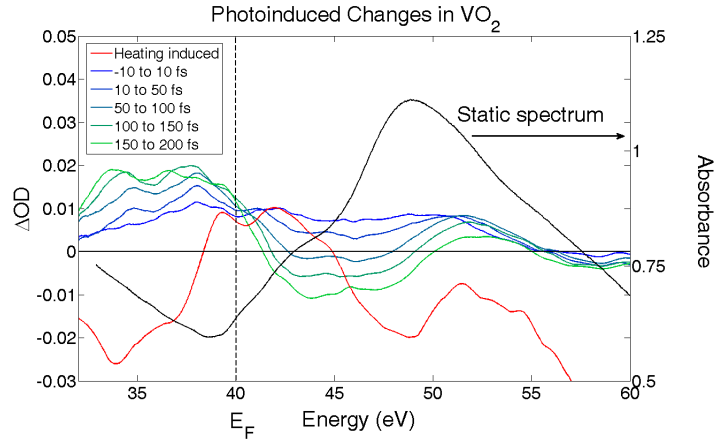


Figure 8: A comparison of photoinduced changes at different delay times with the static absorption spectrum and thermally induced changes.

Apart from this common feature, the excited state that is sampled differs significantly from the spectrum of the thermally induced rutile metallic phase (see Fig. 8), exhibiting higher absorbance below 40 eV and a smaller magnitude of changes above 45 eV. These results suggest the IMT may proceed more quickly than previously thought, and the results highlight the importance of transient, intermediate states immediately following photoexcitation.

5. Attosecond-resolved imaging of the plasmon electric field in metallic nanoparticles

Models of possible experiments where an attosecond light pulse is used to eject electrons from a metal nanosphere, in which a plasmon has been excited by a few-cycle optical pulse, were theoretically explored [6]. The simulations indicate that the plasmon electric field will introduce several features in both velocity map images (VMI) and time-of-flight (TOF) photoelectron velocity traces that directly report the build-up, oscillation, and decay of the plasmon electric field. In these simulations, streaking of photoelectrons emitted from silver nanospheres by 140 attosecond pulses and excited by 5-fs NIR and visible light pulses was computed; these parameters are similar to those that can be obtained with the instruments built using NSSEFF funding.

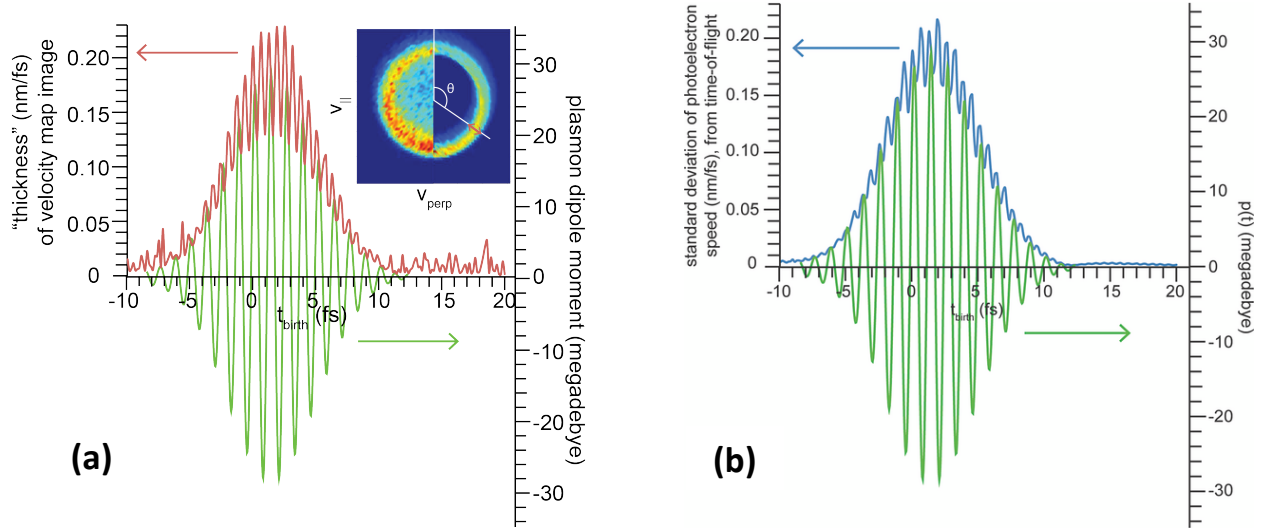


Figure 9: Simulated reconstruction of the dynamical plasmon dipole moment of 80 nm silver nanospheres excited by a resonant 5-fs, 376 nm laser pulse using VMI (a) and ToF (b) techniques. (a) Plot of the breadth of the photoelectron final velocity distribution, inline image, versus time (red, left axis) and plasmon dynamical dipole moment amplitude (green, right axis). As shown in the inset, θ is the angle between the photoelectron final velocity and the laser polarization direction, and the inline image is the average over all θ of the breadth illustrated by the red double-headed arrow. (b) Plot of the standard deviation in speed measured using an electron time-of-flight with a 30° full cone collection angle about the plasmon polarization axis versus time (blue, left axis) and plasmon dynamical dipole moment amplitude (green, right axis).

The analysis showed that conventional VMI analysis by means of Legendre polynomial decomposition is not nearly as successful in reconstructing the plasmon dynamics as the width of the image intensity profile (see Fig. 9). Similarly, the width of the TOF streaking trace will be more useful in reconstructing the plasmon dynamics than the mean of the measured velocity distribution, from which it is difficult to separately attribute laser and plasmon electric field contributions. An advantage of using VMI for plasmon electric field reconstruction was discovered through these simulations: for aligned non-spherical nanostructures, the velocity map images will reflect the spatial distribution of the plasmon electric field, enabling spatial and temporal reconstruction of its dynamics.

It was found that the wide distribution of angles with respect to surface normal at which the photoelectrons can escape the nanostructure surface results in a correlation between the final electron velocity direction and the region of the nanostructure from which it originates. This property arises on the nanoscale because the inelastic mean free path (~ 0.5 nm) of the primary photoelectrons inside the nanostructures is very small compared to the dimensions of the nanostructures. This correlation is useful for reconstructing not only the build-up and decay of the plasmon electric field in time, but also its spatial distribution. Velocity map imaging may be ideal to measure directly the temporal build-up and decay of the plasmon dipole moment amplitude for monodisperse nanospheres or aligned non-spherical nanostructures with attosecond temporal resolution and sensitivity to nanostructure aspect ratio and orientation.

References:

1. S. R. Leone, C. W. McCurdy, J. Burgdorfer, L. Cederbaum, Z. Chang, M. Dudovich, J. Feist, C. Greene, M. Ivanov, R. Kienberger, U. Keller, M. Kling, Z.-H. Loh, T. Pfeiffer, A. N. Pfeiffer, R. Santra, K. Schafer, A. Stolow, W. Thumm, and M. Vrakking, "Attosecond science - what will it take to observe processes in 'real time'," *Nature Photonics* **8**, 162 (2014).
2. H. Mashiko, M. J. Bell, A. R. Beck, M. J. Abel, P. M. Nagel, C. P. Steiner, J. Robinson, D. M. Neumark, and S. R. Leone, "Tunable frequency-controlled isolated attosecond pulses characterized by either 750 nm or 400 nm wavelength streak fields," *Opt. Exp.* **18**, 25887 (2010).
3. E. Goulielmakis, Z.-H. Loh, A. Wirth, R. Santra, M. Rohringer, V. S. Yakovlev, S. Zherebtsov, T. Pfeifer, A. M. Azzeer, M. F. Kling, S. R. Leone, and F. Krausz, "Real-time observation of valence electron motion", *Nature* **466**, 739 (2010).
4. J. Vura-Weis, C.-M. Jiang, C. Liu, H. Gao, J. M. Lucas, F. M. F. de Groot, P. Yang, A. P. Alivisatos, and S. R. Leone, "Femtosecond M_{2,3}-edge spectroscopy of transition-metal oxides: photoinduced oxidation state change in α -Fe₂O₃," *J. Phys. Chem. Lett.* **4**, 3667 (2013).
5. M. Schultze, K. Ramasesha, C. D. Pemmaraju, S. A. Sato, D. Whitmore, A. Gandman, J. S. Prell, L. J. Borja, D. Prendergast, K. Yabana, D. M. Neumark, and S. R. Leone, "Attosecond band-gap dynamics in silicon," *Science* **346**, 1348 (2014).
6. J. S. Prell, L. J. Borja, D. M. Neumark, and S. R. Leone, "Simulation of attosecond-resolved imaging of the plasmon electric field in metallic nanoparticles," *Ann. Phys. (Berlin)*, **525**, 151 (2013).
7. D. C. Koningsberger, R. Prins, Eds., *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES* (Wiley-Interscience, New York, ed. 1, 1988).
8. Popmintchev, T.; Chen, M.-C.; Arpin, P.; Murnane, M. M.; Kapteyn, H. C. The Attosecond Nonlinear Optics of Bright Coherent X-ray Generation, *Nature Photonics* **4**, 822 (2010).
9. Mashiko, H. *et al.* Double optical gating of high-order harmonic generation with carrier-envelope phase stabilized lasers, *Phys. Rev. Lett.* **103**, 183901 (2009).

Publications Acknowledging NSSEFF support:

1. A. R. Beck, D. M. Neumark, and S. R. Leone, "Probing ultrafast dynamics with attosecond transient absorption," *Chem. Phys. Lett.* **624**, 119 (2015).
2. M. Schultze, K. Ramasesha, C.D. Pemmaraju, S.A. Sato, D. Whitmore, A. Gandman, James S. Prell, L. J. Borja, D. Prendergast, K. Yabana, D. M. Neumark, and S. R. Leone, "Attosecond band-gap dynamics in silicon", *Science*, **346**, 1348 (2014).
3. A. R. Beck, B. Bernhardt, E. R. Warrick, M. Wu, S. Chen, M. B. Gaarde, K. J. Schafer, D. M. Neumark and S. R. Leone, "Attosecond transient absorption probing of electronic superpositions of bound states in neon: detection of quantum beats", *New J. Phys.* **16**, 113016 (2014).
4. C-M. Jiang, L. R. Baker, J. M. Lucas, J. Vura-Weis, A. P. Alivisatos, and S. R. Leone, "Characterization of Photo-Induced Charge Transfer and Hot Carrier Relaxation Pathways in Spinel Cobalt Oxide (Co_3O_4)", *J. Phys. Chem. C* **118**, 22774 (2014).
5. L. R. Baker, C-M. Jiang, S. T. Kelly, J. M. Lucas, J. Vura-Weis, M. K. Gilles, A. P. Alivisatos, and S. R. Leone, "Charge Carrier Dynamics of Photoexcited Co_3O_4 in Methanol: Extending High Harmonic Transient Absorption Spectroscopy to Liquid Environments", *Nano Lett.* **14**, 5883 (2014).
6. S. G. Sayres, E. R. Hosler, and S. R. Leone, "Exposing the Role of Electron Correlation in Strong-Field Double Ionization: X-ray Transient Absorption of Orbital Alignment in Xe^+ and Xe^{2+} ", *J. Phys. Chem. A* **118**, 8614, (2014).
7. K. R. Siefertmann, C. D. Pemmaraju, S. Neppl, A. Shavorskiy, A. A. Cordones, J. Vura-Weis, D. S. Slaughter, F. P. Sturm, F. Weise, H. Bluhm, M. L. Strader, H. Cho, M-F. Lin, C. Bacellar, C. Khurmi, J. Guo, G. Coslovich, J. S. Robinson, R. A. Kaindl, R. W. Schoenlein, A. Belkacem, D. M. Neumark, S. R. Leone, D. Nordlund, H. Ogasawara, O. Krupin, J. J. Turner, W. F. Schlotter, M. R. Holmes, M. Messerschmidt, M. P. Minitti, S. Gul, J. Z. Zhang, N. Huse, D. Prendergast, and O. Gessner, "Atomic-Scale Perspective of Ultrafast Charge Transfer at a Dye-Semiconductor Interface", *J. Phys. Chem. Lett.* **5**, 2753 (2014).
8. N. Nijem, H. Bluhm, M. Kunz, S. R. Leone, and M. K. Gilles, " Cu^{1+} in HKUST-1: selective gas adsorption in the presence of water", *Chem. Commun.* **50**, 10144 (2014).
9. S. R. Leone, C. W. McCurdy, J. Burgdörfer, L. S. Cederbaum, Z. Chang, N. Dudovich, J. Feist, C. H. Greene, M. Ivanov, R. Kienberger, U. Keller, M. F. Kling, Z-H. Loh, T. Pfeifer, A. N. Pfeiffer, R. Santra, K. Schafer, A. Stolow, U. Thumm, M. J. J. Vrakking, "What will it take to observe processes in 'real time'?", *Nature Photonics* **8**, 162 (2014).

10. B. Bernhardt, A. R. Beck, X. Li, E. R. Warrick, M. J. Bell, D. J. Haxton, C. W. McCurdy, D. M. Neumark, and S. R. Leone, “High-spectral-resolution attosecond absorption spectroscopy of autoionization in xenon,” *Phys. Rev. A* **89**, 023408 (2014).
11. H. Mashiko, M. J. Bell, A. R. Beck, D. M. Neumark and S. R. Leone, “Frequency Tunable Attosecond Apparatus,” *Springer Series in Chem. Phys.* **106**, 49 (2014).
12. M-F. Lin, D. M. Neumark, O. Gessner, and S. R. Leone, “Ionization and dissociation dynamics of vinyl bromide probed by femtosecond extreme ultraviolet transient absorption spectroscopy”, *J. Chem. Phys.* **140**, 064311 (2014).
13. A. N. Pfeiffer, M. J. Bell, A. R. Beck, H. Mashiko, D. M. Neumark, and S. R. Leone, “Alternating absorption features during attosecond-pulse propagation in a laser-controlled gaseous medium”, *Phys. Rev. A* **88**, 051402. (2013).
14. J. Vura-Weis, C-M. Jiang, C. Liu, H. Gao, J. M. Lucas, F. M. F. de Groot, P. Yang, A. P. Alivisatos, and S. R. Leone, “Femtosecond $M_{2,3}$ -Edge Spectroscopy of Transition Metal Oxides: Photoinduced Oxidation State Change in α - Fe_2O_3 ”, *J. Chem. Phys. Lett.* **4**, 3667 (2013).
15. M. J. Bell, A. R. Beck, H. Mashiko, D. M. Neumark, and S. R. Leone, “Intensity dependence of light-induced states in transient absorption of laser-dressed helium measured with isolated attosecond pulses”, *J. Mod. Optic.* **60**, 1506 (2013).
16. E. R. Hosler and S. R. Leone, “Characterization of vibrational wave packets by core-level high-harmonic transient absorption spectroscopy,” *Phys. Rev. A*, **88**, 023420 (2013).
17. J. S. Prell, L. J. Borja, D. M. Neumark, and S. R. Leone, “Attosecond-resolved imaging of the plasmon electric field in metallic nanoparticles,” *Ann. Physik—Berlin* **525**, 151 (2013).
18. Z-H. Loh and S. R. Leone, “Capturing ultrafast quantum dynamics with femtosecond and attosecond x-ray core-level absorption spectroscopy,” *J. Phys. Chem. Lett.* **4**, 292 (2013).
19. A. N. Pfeiffer, S. G. Sayres, and S. R. Leone, “Calculation of valence electron motion induced by sequential strong field ionization,” *Mol. Phys.* **111**, 2283 (2013).
20. H. A. Chen, C. L. Hsin, Y. T. Huang, M. L. Tang, S. Dhuey, S. Cabrini, W. W. Wu, and S. R. Leone, “Measurement of Interlayer Screening Length of Layered Graphene by Plasmonic Nanostructure Resonances,” *J. Phys. Chem. C* **117**, 22211 (2013).
21. P. M. Nagel, J. S. Robinson, B. Harteneck, T. Pfeifer, M. J. Abel, J. S. Prell, D. M. Neumark, R. A. Kaindl, and S. R. Leone, “Surface plasmon assisted electron acceleration in photoemission from gold nanopillars,” *Chem. Phys.* **414**, 106 (2012).
22. A. N. Pfeiffer and S. R. Leone, “Transmission of an isolated attosecond pulse in a strong-field dressed atom,” *Phys. Rev. A*, **85**, 053422 (2012).

23. S. H. Chen, M. J. Bell, A. R. Beck, H. Mashiko, M. X. Wu, A. N. Pfeiffer, M. B. Gaarde, D. M. Neumark, S. R. Leone, and K. J. Schafer, "Light-induced states in attosecond transient absorption of laser-dressed helium," *Phys. Rev. A*, **86**, 063408 (2012).
24. M-F. Lin, A. N. Pfeiffer, D. M. Neumark, S. R. Leone, and O. Gessner, "Strong-field induced XUV transmission and multiplet splitting in $4d^{-1}6p$ core-excited Xe studied by femtosecond XUV transient absorption spectroscopy," *J. Chem. Phys.* **137**, 244305 (2012).

Publications in press

N. Nijem, K. Fuersich, S. Kelly, C. Swain, S. R. Leone, and M. K. Gilles, "HKUST-1 thin film layer-by-layer liquid phase epitaxial growth: film properties and stability dependence on layer number," *Cryst. Growth Des.*, (in press) (2015).

X. Li, B. Bernhardt, A. R. Beck, E. Warrick, A. Pfeiffer, M. J. Bell, D. Haxton, C. McCurdy, D. M. Neumark, and S. R. Leone, "Investigation of coupling mechanisms in attosecond transient absorption of auto-ionizing states: comparison of theory and experiment in xenon," *J. Phys. B: At. Mol. Opt. Phys.* (in press) (2015).

K. Ramasesha, S. R. Leone, and D. M. Neumark, "Real-time probing of electron dynamics using attosecond time-resolved spectroscopy," *Annu. Rev. Phys. Chem.* (Invited, submitted) (2015).

Invited Presentations:

1. "Ultrafast and attosecond x-ray investigations of molecular dynamics," 17th National Congress Meeting, Ciudad Universitaria, Córdoba, Argentina, May 2011.
2. "Attosecond electron dynamics," Physical Chemistry Colloquium, University of Maryland, College Park, MD, September 2011.
3. "Time and chemical dynamics: from attoseconds to x-rays," Physical Chemistry Colloquium, Princeton University, Princeton, NJ, February 2012.
4. "Time for chemical dynamics: from x-rays to attoseconds," Physical Chemistry Colloquium, Massachusetts Institute for Technology, Cambridge, MA, February 2012.
5. "Advanced light sources for analytical spectroscopy: from x-rays to attoseconds," Physical Chemistry Colloquium, University of the Pacific, Stockton, CA, February 2012.
6. "Time and chemical dynamics: from x-rays to attoseconds," Physical Chemistry Colloquium, University of Victoria, Victoria, BC, Canada, March 2012.
7. "Attosecond electron dynamics in atoms and molecules," Lectures in Modern Chemistry Series, Charles A. McDowell Lecture, The University of British Columbia, Vancouver, BC, Canada, March 2012.

8. "Probing of molecular dynamics in the attosecond limit," Physical Chemistry Colloquium, Simon Fraser University, Burnaby, BC, Canada, March 2012.
9. "Attosecond transient absorption and photoemission for plasmonics and semiconductors," AFOSR Workshop on Attosecond Science and Engineering, University of Central Florida, Orlando, FL, April 2012.
10. "Time for chemical dynamics: from x-rays to attoseconds," Faculty Colloquium, Distinguished Schulich Lecture, Technion – Israel Institute of Technology, Haifa, Israel, June 2012.
11. "Charge state dynamics of semiconducting and plasmonic nanosystems," Physical Chemistry Colloquium, Technion – Israel Institute of Technology, Haifa, Israel, June 2012.
12. "Tracking electron and nuclear dynamics with femtosecond/attosecond x-ray spectroscopy," Ultrafast Dynamic Imaging of Matter Conference, Banff Centre, Banff, Alberta, Canada, July 2012.
13. "X-ray investigations of electron dynamics toward the attosecond limit," Atomic & Molecular Interactions Gordon Research Conference, Stonehill College, Easton, MA, July 2012.
14. "Femtosecond and attosecond x-ray spectroscopy of molecular dynamics," Electronic Spectroscopy & Dynamics Gordon Research Conference, Bates College, Lewiston, ME, July 2012.
15. "Molecular dynamics in the attosecond limit," Physical Chemistry Colloquium, Indiana University, Bloomington, IN, August 2012.
16. "Isolated attosecond pulse probing of atomic and molecular dynamics," 44th Annual APS Division of Atomic, Molecular, and Optical Physics (DAMOP) Meeting, Centre des Congrès de Québec, Québec City, Québec, Canada, June 2013.
17. "Probing of atomic and molecular dynamics with attosecond pulses," CLEO: 2013 Conference, San Jose Convention Center, San Jose, CA, June 2013.
18. "High-harmonic isolated attosecond pulse transient absorption probing of atomic and molecular dynamics," The 11th Edition of the Femtochemistry Conference (FEMTO11), Technical University of Denmark, Copenhagen, Denmark, July 2013.
19. "Attosecond probing of atomic and molecular dynamics," Frontiers in Chemistry Colloquium, Wayne State University, Detroit, MI, September 2013.
20. "Attosecond transient absorption of field-manipulated excited states," 2013 Frontiers in Optics/Laser Science 97th Annual Meeting, Hilton Bonnet Creek, Orlando, FL, October 2013.
21. "Attosecond probing of chemical dynamics," 17th Annual Southeast Ultrafast Conference, Louisiana State University, Baton Rouge, LA, January 2014.
22. "Attosecond probing of atomic, molecular, and solid state dynamics," University of Arizona, Tucson, AZ, March 2014.

23. "Isolated x-ray attosecond pulses and the science of attosecond measurements," International Conference on X-Ray Lasers, Colorado State University, Fort Collins, CO, May 2014.
24. "Attosecond transient absorption: from atoms to band gap solids," Multiphoton Processes Gordon Research Conference, Bentley University, Waltham, MA, June 2014.
25. "Charge state dynamics of semiconducting nanosystems," Colloidal Semiconductor Nanocrystals Gordon Research Conference, Bryant University, Smithfield, RI, July 2014.
26. "Attosecond electronic band dynamics," 2014 OSA Frontiers in Optics/Laser Science Conference, Tucson, AZ, October 2014.
27. "Attosecond transient absorption: from atoms to band gap solids," 55th Sanibel Symposium, University of Florida, St. Simons Island, GA, February 2015.
28. "Attosecond transient absorption: from atoms to band gap solids," Physical Chemistry Colloquium, University of Texas, San Antonio, TX, March 2015.

AFOSR Deliverables Submission Survey

Response ID:4552 Data

1.

1. Report Type

Final Report

Primary Contact E-mail

Contact email if there is a problem with the report.

srl@berkeley.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

5106435467

Organization / Institution name

University of California Berkeley

Grant/Contract Title

The full title of the funded effort.

(NSSEFF) Attosecond Electron Processes in Materials: Excitons, Plasmons, and Charge Dynamics

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-10-1-0195

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Stephen R. Leone

Program Manager

The AFOSR Program Manager currently assigned to the award

Evelyn Dohme

Reporting Period Start Date

05/01/2010

Reporting Period End Date

04/30/2015

Abstract

A five year program focusing on investigation of attosecond electron dynamics in solid state materials is completed. Two experimental apparatuses for attosecond time-resolved extreme ultraviolet (XUV) studies were constructed. Highlights of results are: a 450 attosecond electronic response time in the conduction band of silicon was experimentally measured by observing steps in the L2,3-edge spectrum of silicon, synchronized with the excitation laser electric field. Independent electron and hole dynamics were observed in germanium by time-resolved ultrafast measurements on the M4,5-edge spectrum of germanium. A near-instantaneous spectral response over a broad range around the vanadium M2,3-edge, followed by a fast reshaping of the spectrum, was observed in VO₂, suggesting a signature of the ultrafast insulator to metal transition.

Distribution Statement

This is block 12 on the SF298 form.

Distribution A - Approved for Public Release

Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

SF298 Form

Please attach your [SF298](#) form. A blank SF298 can be found [here](#). Please do not password protect or secure the PDF. The maximum file size for an SF298 is 50MB.

[SF 298_NSSEFF_FA9550-10-1-0195_final.pdf](#)

Upload the Report Document. File must be a PDF. Please do not password protect or secure the PDF. The maximum file size for the Report Document is 50MB.

[NSSEFF final report 2015 Leone 5.9.15.pdf](#)

Upload a Report Document, if any. The maximum file size for the Report Document is 50MB.

Archival Publications (published) during reporting period:

see report

Changes in research objectives (if any):

none

Change in AFOSR Program Manager, if any:

none

Extensions granted or milestones slipped, if any:

none

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

E-mail user

May 09, 2015 16:27:00 Success: Email Sent to: srl@berkeley.edu
